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<b>(54) Title:</b> SOLVENTLESS POLYURETHANE SPRAY COMPOSITIONS AND METHOD FOR APPLYING THEM  <b>(57) Abstract</b>  A method for preparing polyurethane by spraying solventless, equal volume mixtures of: (a) a liquid polyisocyanate; polyisocyanurate or isocyanate terminated quasi-prepolymer; and (b) a curing agent comprised of a blend of from about 0 to 15 % of a polyamine having an equivalent weight from about 30 to about 200, about 10 to 20 % of a low molecular weight glycol having an equivalent weight of from about 30 to 200, about 40 to 80 % of a relatively high molecular weight polyol or polyamine having an equivalent weight of about 350 to 2000, and about 1 to 20 % of a synthetic zeolite molecular sieve, wherein the average equivalent weight of (b) is from about 150 to 500.		

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SOLVENTLESS POLYURETHANE SPRAY COMPOSITIONS AND  
METHOD FOR APPLYING THEM

Field of the Invention

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This invention pertains to two-component solventless spray compositions for producing polyurethane and poly(urea)urethane coatings, the products produced from these compositions, a process for producing such products, and methods for using them.

Background of the Invention

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Polyurethane coatings are well known and have gained commercial acceptance as protective and decorative coatings for metal, wood, concrete, foam, and plastics in the aircraft, construction, product-finishing, textile and maintenance/architectural coatings markets. The basic raw materials used to prepare these coatings generally comprise as essential components (a) an aliphatic or aromatic di-or-polyisocyanate and (b) a co-reactant or curative component bearing active hydrogen containing groups, i.e., hydroxyl or amine groups, or latent active hydrogen containing groups, e.g., oxazolidines or ketimines. For typical two-package coating systems, the co-reactant is usually a hydroxyl group containing oligomer chosen from the general classes of polyesters, polyethers, alkyd resins and acrylics.

1 The co-reactant component is generally the vehicle for  
pigment (grinding) and may also contain other additives  
such as catalysts, plasticizers, bitumenous extenders,  
suspending agents, anti-skinning agents, surfactants, and  
5 rheological modifiers.

Both the isocyanate-containing component and the  
active hydrogen-containing co-reactant usually contain  
volatile organic solvents whose primary function is to  
lower viscosity thereby providing a consistency suitable  
10 for spray application with conventional air, airless and  
electrostatic spray equipment.

A growing emphasis on compliance with government  
environmental and health hazard regulations that limit  
both the type and amount of volatile organic compounds  
(VOC) has prompted coating manufacturers and end users to  
15 evaluate new coating technologies.

Prior art high solids and solventless polyurethane  
coatings have been developed which comply with solvent  
emission regulations. As used herein, a solventless  
polyurethane coating is one in which substantially all of  
20 the constituents remain in the applied coating.

The first solventless, urethane coatings were the  
"one shot" systems, so named because no prereaction of  
components is involved. Typical "one shot" systems  
consist of a pure isocyanate component, usually  
25 4,4'-diphenylmethane diisocyanate (MDI), and a curative  
component comprised of a blend of active hydrogen  
containing co-reactants, for example polyether or  
polyester polyols and lower MW glycol, with fillers and  
catalyst. The components are usually combined at  
30 volumetric mix ratios of 1:1 to 4:1. Although coating  
systems of this type are sprayable without the use of a  
solvent, there are some disadvantages. One shot systems  
are moisture sensitive because they contain a very high  
percentage of unreacted diisocyanate, usually 26-31% by  
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1 weight, and cannot be sprayed under humid conditions  
without blowing or foaming. Another major disadvantage  
of one shot spray systems is reflected in the low  
physical properties of the polyurethanes they produce.  
5 Important physical properties such as tensile and tear  
strength and abrasion resistance are inferior to those  
obtained by solvent containing systems.

Prior art two package, solventless polyurethane  
coating systems with superior physical properties have  
also been developed. These spray systems are generally  
based on an isocyanate-containing prepolymer component  
combined with a curative component comprised of a  
viscous, sometimes solid, polyamine whose viscosity has  
been reduced by addition of a non-volatile diluent or  
whose volume has been adjusted with "polyol" so that it  
15 can be combined with the isocyanate component at  
predetermined volumetric mix ratios.

U.S. Patent 4,195,148 and U.S. Patent 4,234,445  
disclose solventless polyurethane coatings which use a  
non-reactive, non-volatile lactone viscosity modifier to  
20 dissolve viscous or solid prepolymer and curative  
components to reduce viscosity of the systems so that  
they may be applied using airless, plural-component spray  
equipment.

25 U.S. Patent 4,267,299 also discloses sprayable,  
solventless polyurethane compositions which combine an  
isocyanate terminated prepolymer component (Part A) with  
a curative component (Part B). The curative component is  
a blend of highly reactive polyamine with a slower  
reacting, higher molecular weight (MW) polyol. Part B  
30 includes enough highly reactive polyamine to react with  
substantially all of the isocyanate groups in the Part A  
within 2 to 5 minutes. The higher MW polyol is present  
in relatively small amounts and functions as a "reactive  
filler" or bulking agent which allows the Part A and Part  
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1 B to be combined in ratios of from 2:1 to 4:1.

1 The polyurethane produced from preferred embodiments  
of prepolymer-based, prior-art inventions (U.S.  
4,195,148, U.S. 4,234,445 and U.S. 4,267,299) have  
5 superior physical properties such as tensile strength,  
tear strength, and abrasion resistance compared to  
one-shot, solventless coating systems. Moreover, such  
prepolymer-based solventless coating systems are  
generally less sensitive to moisture than one-shot  
10 solventless systems because pre-reaction of the  
isocyanate with polyol to form the prepolymer component  
results in less reactive isocyanate, typically 3 to 12%  
by weight.

15 There are some disadvantages associated with prior  
art, prepolymer based solventless polyurethane coatings.  
For optimum mixing, a ratio of 1:1 is desirable;  
preferred embodiments of the prior art have volumetric  
mix ratios of 3:1. A major disadvantage of preferred  
20 embodiments of prior-art, prepolymer-based, solventless,  
polyurethane coatings is that the components must be  
heated to 160°F - 200°F to reduce viscosities for spray  
application. Heating, maintaining and applying  
components at 160 - 200°F requires additional equipment  
such as drum heaters to warm viscous materials to a  
25 pumpable viscosity, electrical induction heaters to  
further raise component temperatures and reduce  
viscosity, and the use of heated hoses to maintain  
temperature until the components enter the spray gun.  
Prior-art systems have fast gel times, typically 0.5 to 3  
30 minutes at application temperatures of 160 - 200°F, and  
must be applied with an internal mix, plural-component  
spray gun such as the Binks 43-P. Internal mix spray  
guns of this type are connected to three spray hoses; one  
for each component and one for solvent flushing. The  
35 hoses increase the weight of the spray gun, make the gun

1       awkward to use, and severely restrict the movement of the  
applicator in confined areas such as manholes or covered  
hopper cars. Accordingly, a solventless, polyurethane  
coating composition is needed which combines the ease of  
5       application at ambient temperatures and superior physical  
properties.

#### Summary of the Invention

10       The two component, solventless spray composition for  
producing polyurethane and poly(urea)urethane coatings of  
the present invention includes substantially equal  
volumes of an isocyanate-containing component and a  
curative component. The isocyanate-containing component  
comprises a liquid polyisocyanate, polyisocyanurate or  
15       isocyanate-terminated prepolymer or quasi-prepolymer.  
The curative component is comprised of from about 0% to  
about 15% by weight of one or more polyamines  
(di-or-polyamines) or alkanolamines in an amount  
sufficient to react to form a thixotropic mixture about  
20       15 seconds to about 2 minutes after being mixed with the  
isocyanate-containing component, from about 10% to about  
20% by weight of one or more glycols having an equivalent  
weight in the range from about 30 to about 200, from  
about 40% to about 80% by weight of one or more high  
25       molecular weight polyols or polyamines having an  
equivalent weight in the range from about 300 to about  
2000, and from about 1% to about 20% by weight of one or  
more additives to adsorb moisture or carbon dioxide.

30       The polyamines or alkanolamines preferably have an  
equivalent weight in the range from about 30 to about 200  
and are present in an amount sufficient to form a coating  
which is substantially tack-free within about 5 minutes  
to about 60 minutes after being mixed with the  
isocyanate-containing component. In a specifically  
35       preferred embodiment, the polyamines or alkanolamines

1 make up from about 2% to about 7% by weight of the  
curative component and are diethyl toluenediamine.

5 The curative component can also include one or more  
catalysts to promote the hydroxyl-isocyanate reaction in  
formation of a polyurethane or poly(urea)urethane.  
Preferably the two components have an isocyanate to  
active hydrogen equivalent ratio of from about 0.85 to  
about 1.15. When the components are blended with a  
pigment and/or other additives or fillers the blend  
10 preferably has an average equivalent weight of from about  
150 to about 500. These optional pigments and/or other  
additives or filler are part of the curative component  
prior to blending.

15 The present invention also encompasses a method  
wherein the isocyanate-containing component and curative  
component are separately delivered to a manifold,  
preferably in a volumetric ration of 1:1. The components  
are then mixed with each other and sprayed through an  
atomizing nozzle onto a surface to produce a polyurethane  
or poly(urea)urethane coating. For spraying the mixture  
20 at ambient temperatures, around 70°F to 100°F, the  
isocyanate-containing component and the curative  
component preferably have viscosities less than 1000  
centipoise at these temperatures.

#### 25 Objects of the Invention

This invention provides solventless, polyurethane  
coating compositions which combine the ambient  
temperature ease of applying solventless, one-shot  
polyurethane coating systems with the lower moisture  
30 sensitivity and superior physical properties of the  
coatings produced from solventless, prepolymer-based  
polyurethane coating compositions.

Preferably, the coating system of this invention  
includes Parts A and B which are mixed substantially 1:1  
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1 by volume.

5 Preferably, Part B (the curative component) comprises essentially a major portion of a blend of high molecular weight polyol or polyamine and low molecular weight glycol, a minor portion of a highly reactive alkanolamine or polyamine, and an additive to adsorb moisture and CO<sub>2</sub>. Preferably, Part B also produces a thixotropic mixture approximately 30 seconds after being combined with the Part A (the isocyanate-containing component). This thixotropic mixture can be spray-  
10 applied to thicknesses of from 20-250 mils on vertical surfaces without sagging even though it is applied at ambient temperature, and it is tack-free in 5-60 minutes.

15 In the preferred spraying method of this invention, the Part A and Part B components are pumped from separate containers into a manifold where they are mixed 1:1 by volume, and then delivered through a single "whip-hose" to a spray nozzle for application to the surface to be coated.  
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Detailed Description of the Invention

1        This invention provides two-component, solventless  
polyurethane compositions which may be combined at  
substantially 1:1 by volume, and applied with  
5       commercially available, plural component, airless-spray  
equipment at ambient temperatures.

      The Part A, or isocyanate-containing component,  
includes a liquid polyisocyanate, polyisocyanurate, or  
isocyanate-terminated prepolymer or quasi-prepolymer with  
10       a reactive isocyanate content of from about 12-25% by  
weight. Quasi-prepolymers useful in this invention are  
materials made by reacting a polyurethane forming polyol  
or polyamine with an excess of a polyurethane forming  
aliphatic or aromatic polyisocyanate such as poly-  
15       methylene polyphenyl isocyanate, 4,4'-diphenylmethane  
diisocyanate (MDI), and liquid carbodiimide or  
uretonimine modified MDI variants. Other useful  
isocyanates include:       3-isocyanatomethyl-3,5,5,  
-trimethylcyclohexyl isocyanate (IPDI); bis  
20       (4-isocyanatocyclohexyl) methane (Desmodur W); xylene  
diisocyanate (XDI); m-and-p-tetramethyl xylene  
diisocyanate (m-and-p-TXMDI); "dimeryl" diisocyanate  
(DDI); and adducts or trimers of hexamethylene  
diisocyanate with free monomeric isocyanate content less  
25       than 0.7% such as Desmodur N3200 and N3300. Toluene  
diisocyanate (TDI) adducts with free monomeric TDI  
content of less than 0.7% may also be employed.

      The polyol or polyamines used to make the  
quasi-prepolymer are poly(alkylene ether) glycols,  
30       polyester glycols, polycaprolactone glycols,  
polycarbonate glycols, castor oils, polybutadiene  
glycols, polyether-thioether-glycols and the like of  
which the following are mentioned as non-limiting  
examples:

35       polytetramethylene ether glycols, MW 650-2900

1 polypropylene ether glycols, MW 400-4000  
castor oil and castor oil derivatives, MW 300-1000  
polycaprolactone glycols, MW 300-2000  
polydiethylene adipate, MW 500-2000  
5 hydroxyl-terminated Bisphenol A polyols, MW 400-1000  
polycarbonate glycols, MW 500-2500  
polybutylene and ethylene/butylene adipate, MW  
500-2000

polyetherthioether glycols, MW 400-2000  
10 hydroxyl functional acrylic polyols, MW 300-1000

The second component of the present invention is a  
Part B or curative component which is preferably  
comprised of:

- 15 (a) 0 to 15% by weight of a polyamine (di-or-polyamine)  
or an alkanolamine with an equivalent weight of 30  
to 200;  
(b) 10 to 20% by weight of a glycol having an equivalent  
weight of from 30 to 200;  
(c) 40 to 80% by weight of a high molecular weight  
20 polyol or polyamine with equivalent weight of from  
300-2000; and  
(d) 1 to 20% by weight of an additive to adsorb moisture  
or CO<sub>2</sub>.

These are blended to have an average equivalent weight of  
25 from 150 to 500.

The curative component may also contain pigments or  
dyes, rheological additives, surfactants, UV stabilizers,  
and fillers such as silica or silica flour, barytes,  
talc, aluminum trihydrate, calcium carbonate and the  
like. Catalysts which promote the hydroxyl-isocyanate  
30 reaction in formation of a polyurethane are highly  
desirable constituents of the curative component.  
Catalysts well known in the art include such materials as  
dibutyltin dilaurate, stannous octoate, lead octoate,  
phenylmercuric proprionate, ferric acetylacetonate and  
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1       organo-zinc compounds such as zinc octoate. The  
preferred catalyst is the composition Cotin 222 sold by  
Cosan Chemical Corporation. Cotin 222 is an organo-tin  
5       carboxylate containing negligible free acid and is  
described in detail in U.S. Patent No. 3,661,887, which  
is incorporated herein by reference. Coscat 83, a  
proprietary organo-metallic composition based on bismuth  
and sold by Cosan Chemical Corp., can also be used.  
Catalysts are particularly desirable when the  
10       polyurethane coatings are applied in the presence of  
moisture. The catalyst promotes the hydroxyl-isocyanate  
reaction in favor of the reaction of isocyanate with  
water so that the superior physical properties of the  
coating are maintained.

15       Catalysts also act to accelerate the cure time of  
the coating and allow application to vertical surfaces  
without sagging. In fact, if enough catalyst is added to  
the curative component of this invention, the percent by  
weight of polyamine or alkanolamine used in the curative  
20       component can be reduced to zero. However, this does not  
result in the most preferable coating because the  
physical properties of the coating suffer somewhat when  
the percent by weight of polyamine or alkanolamine is  
reduced below two.

25       The following are non-limiting illustrative examples  
of essential constituents of the curative or Part B  
component:

30       Polyamines or alkanolamines with equivalent weight  
of 30 to 200 include triethanolamine, 1,6-hexanediamine,  
Quadrol (BASF), methylene dianiline, menthanediamine,  
isophorone diamine, 1,4-diamino cyclohexane, Lauramin  
C-260 (BASF), PACM-20 (Dupont), Jeffamine T400 (Texaco),  
methylene-bis-2,6 diisopropylaniline ("MDPA": from Ethyl  
or "MDIPA": from Lonza), diethyl toluenediamine (DETDA  
35       sold by Ethyl and Lonza), t-butylbenzenediamine,

1 methylene-bis-2, -diethylaniline, 2,2-diaminodiphenyl  
disulphide, 1,3-propanediol di-p-aminobenzoate, bis  
(2-aminophenylthio) ethane, and methylene bis  
5 N-methylantranilate. The type of polyamine or  
alkanolamine selected depends on the  
isocyanate-containing component used to form the  
polyurethane. If the isocyanate component is based on  
aliphatic isocyanate, a very reactive aliphatic or  
cyloaliphatic polyamine such as 1,6-hexanediamine,  
10 PACM-20 sold by Dupont, isophorone diamine or  
menthanediamine is used. If the isocyanate component is  
based on aromatic diisocyanate, aromatic diamines such as  
methylenedianiline, and diethyltoluenediamine may be  
used. The specific amount, if any, of polyamine used  
15 reacts to form a thixotropic mixture approximately 15  
seconds to 2 minutes after mixing with the isocyanate  
containing component, preferably this amount ranges from  
2 to 7% by weight of the curative component.

20 The second preferred constituent of the curative  
component is a glycol or polyol having an equivalent  
weight of from 30 to 200. Useful glycols include  
ethylene glycol, trimethylolpropane, 1,3-butylene glycol,  
1,4-butylene glycol, 2,ethyl-1,3-hexanediol,  
1,5-pentanediol, 1,6-hexanediol, dipropylene glycol,  
25 glycerol, neopentylglycol, thiodiglycol, bisphenol A-and  
bisphenol F-based glycols, dihydroxyethylethers of  
resorcinol and hydroquinone, and low molecular weight  
polyalkylene ether glycols. The presence of the glycol  
in the curative component helps contribute to the low  
30 temperature sprayability of the spray composition.

35 The third preferred constituent of the curative  
component is a relatively high molecular weight polyol or  
polyamine having an equivalent weight of from 300-2000.  
Particularly useful polyols are polytetramethylene ether  
glycol, poly(ethylene oxide)-terminated polypropylene

1 ether glycols, castor oil, polypropylene ether glycols,  
polyethylene-butylene adipate glycols, polybutadiene  
glycols, polyetherthioether glycols and oligomeric  
diaminobenzoates such as Polyamine-1000 sold by Polaroid.

5 The fourth preferred constituent of the curative  
component is a non-reactive additive which reduces  
blistering and blowing or foaming during application of  
the solventless polyurethane coating system in humid  
weather or on damp substrates by combining with or  
10 adsorbing moisture and/or carbon dioxide. Suitable  
moisture scavenging additives are calcium sulfate,  
calcium oxide and synthetic zeolite "molecular sieves".  
The amount of moisture scavenging additive used is  
increased according to the expected humidity at the point  
15 where the coating is to be applied.

Preferably, the low molecular weight polyamine, low  
molecular weight glycol, high molecular weight polyol,  
and moisture-adsorbing additive are blended with pigment,  
catalyst and other additives in Part B (curative) to an  
average equivalent weight of from 150 to 500. The  
20 equivalent weight of the curative blend depends on the  
isocyanate content of the Part A or isocyanate containing  
component, and is calculated to give an isocyanate to  
active hydrogen equivalent ratio of from 0.85 to 1.15  
based on a 1:1 volumetric mixture of Part A to Part B.

25 The isocyanate and curative components typically  
have viscosities of less than 1000 centipoise at 70°F and  
are pumped directly from drums in two separate 3000 psi,  
1/4 inch ID paint hoses to 1:1 proportioning cylinders  
mounted below a 30:1, air-regulated Graco Bulldog pump  
30 which delivers equal volumes of both components to a  
manifold fitted with static mixer. The components are  
thoroughly mixed as they pass through the manifold and  
static mixer into a single, 3/16 inch ID "whip-hose" and  
are delivered to a standard, airless spray gun such as a  
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1 Graco Silver. The mixed components have sufficient  
potlife to permit the use of 25 to 50 feet of whip hose  
and "triggering" of the spray gun to the off position for  
30-45 seconds. The whip hose and standard airless spray  
5 gun is less cumbersome than the three hoses and  
plural-component, internal-mix spray gun used to spray  
prepolymer-based polyurethane coating systems, and is  
easier to use in confined or restricted-access areas.  
Triggering of the spray gun off during the coating  
10 operation often results in less overspray and more  
economical use of material as the gun is moved from a  
sprayed area to a non-sprayed area.

The mixed composition is atomized at the spray gun  
tip and deposited on the surface to be coated at  
15 thicknesses of from 15 to 30 mils per pass. The  
thixotropic mixture permits multiple passes of the spray  
gun and continuous film build up to 250 mils without  
sagging. The applied coating is tack-free in from 5 to  
60 minutes and is ready for service within 4 to 24 hours,  
20 depending on the application.

The coating compositions of the present invention  
exhibit excellent adhesion by themselves to many  
substrates including metal, wood and concrete. A primer  
or adhesive is not required for many applications, if the  
25 substrate has been properly prepared and cleaned.  
Coating compositions of the present invention exhibit  
excellent adhesion to ferrous metal substrates which have  
been sandblasted to a near-white metal finish  
(SSPC-SP-10) with 2-3 mil profile and concrete that has  
30 been sweepblasted or acid-etched. When there is a long  
period of time between blasting the metal and coating or  
where optimum adhesion and corrosion protection are  
desired, primers such as Amerthane<sup>R</sup> 135, Amercoat<sup>R</sup> 2183,  
Amercoat<sup>R</sup> 460, Amercoat<sup>R</sup> 66, and Amerlock<sup>R</sup> 400 should be  
35 used. Concrete with rough surfaces or cracks may be

1 filled with a cementitious coating such as Nu-Klad<sup>R</sup> 965  
or an epoxy-surfacer such as Nu-Klad<sup>R</sup> 114 and then sealed  
with a primer such as Amerthane<sup>R</sup> 135.

5 The solventless polyurethane compositions of this  
invention form polyurethane coatings useful in many  
applications. The isocyanate and curative components are  
selected for a particular application based on the  
physical characteristics and chemical resistance  
10 characteristics of the polyurethane they produce. For  
example, coating systems based on polytetramethylene  
ether glycol are well suited for applications which  
require good resistance to abrasive wear such as  
ore-handling equipment, and hopper cars. Coating systems  
based on castor oil provide good hydrolytic stability and  
15 chemical resistance, such as for wastewater treatment  
ponds and chemical or crude oil storage tanks.

The spray system of this invention has major  
advantages compared to high-solids, solvent-containing  
polyurethane coating systems; solventless, one shot  
polyurethane coating systems; and prior-art solventless,  
20 prepolymer-based polyurethane coating systems.

The major advantages compared to solvent-containing  
systems are:

- 25 1. There are no volatile solvents which present health  
or explosion hazards, and there are no limitations  
arising from environmental regulations on volatile  
organic compound emissions.
2. The spray system of the present invention can, with  
multiple passes, apply high coating thicknesses of  
30 from 20 to 250 mils without sagging compared to 10  
to 40 mils for solvent-containing systems.
3. Tack-free time and curing are short, which allows  
for quick recoating and reduces the time required  
for the applied coating to be handled or placed in  
35 service.



1        4.    The solventless system of the present invention requires less volume to apply the same dry film thickness than a solvent-containing system; there is less material to store, handle, and apply.

5        5.    Problems associated with solvent-containing systems such as shrinkage, blistering, holidays and premature deadhesion caused by solvent retained in the applied coating are significantly reduced.

10       The major advantages of the present invention compared to solventless, one-shot, polyurethane coating systems are reduced sensitivity to moisture-generated foaming, and improved physical properties such as higher tensile and tear strength.

15       Spray compositions of the present invention have equivalent physical properties such as tensile and tear strength compared to prior-art, solventless, prepolymer-based polyurethane systems but have the following major advantages:

20       1.    Spray compositions of the present invention are low viscosity liquids that can be applied at 70°F - 100°F. The need for expensive, additional equipment required to preheat, maintain and apply prepolymer-based coating systems is eliminated.

25       2.    Coating systems of the present invention are applied with a single paint hose and standard, airless spray gun, which is easier to use than the internal-mix, plural-component guns used to apply prior-art, prepolymer-based coating systems.

30       3.    The compositions of the present invention have sufficient pot-life to allow triggering of the spray gun for 30-45 seconds, which reduces overspray and consumes less material when coating complicated shapes.

35       4.    The components of the present invention are combined 1:1 by volume, which is desirable for optimum

1 mixing, and is more forgiving to off-ratio  
conditions which frequently occur during field  
application using plural component, airless spray  
equipment.

5 5. Despite being applied at 70°F - 100°F and requiring  
5 to 60 minutes for the coating to be tack-free, a  
continuous film of up to 250 mils in thickness can  
be applied without sagging so that spray  
10 compositions of the present invention have  
equivalent physical properties compared to  
prior-art, solventless, prepolymer-based  
polyurethane systems applied at higher temperatures  
and having faster cure times.

15 The following examples illustrate, but do not limit,  
the present invention.

#### EXAMPLE I

##### Preparation of An MDI/polypropylene Ether Glycol Quasi-Prepolymer (Part A)

20 7505.0 grams (52.3 eqs) of carbodiimide modified  
MDI, Isonate 143L sold by Upjohn, was charged to a resin  
flask equipped with an agitator, thermometer, N<sub>2</sub> inlet,  
condenser, and an addition funnel. 2450.0 grams (4.9  
eqs) of predried Niox Polyol PPG1025 (%H<sub>2</sub>O content less  
25 than 0.05%) was charged to the addition funnel and added  
to the Isonate 143L with continuous agitation and  
nitrogen blanketing. The exotherm was kept below 50°C by  
adjusting the addition rate. After the addition of Niox  
Polyol PPG1025 was complete, the temperature was raised  
30 to 70°C and held for one hour. Table I shows the  
results.

##### Preparation of the Curative Blend (Part B)

35 The constituents listed below were charged to a  
resin flask equipped as described in the prepolymer  
preparation.

	<u>Ingredients</u>	<u>Parts by Weight (grams)</u>	<u>Equivalents</u>
1	Castor DB Oil, Caschem	4821.0	14.1
	2-ethyl-1,3 hexanediol	1474.0	20.2
	DETDA, Ethyl	636.0	7.1
5	Niax Polyol PPG 1025, Union Carbide	1373.0	2.8
	Baylith L Paste, Mobay	1264.0	1.8
	PDI 47055B, PDI Inc.	406.0	0.2
	Dibutyltindilaurate	3.0	---
10	The ingredients were heated at 100°C under vacuum until the moisture content was less than 0.08% by weight. Table I shows the results.		

EXAMPLE IIPreparation of An MDI/Polytetramethylene Ether Glycol15      Quasi-Prepolymer (Part A)

The same procedure used to prepare Part A in Example I was used except that the components were 11,125.0 grams (82.1 eqs) Rubinate XI-208 from Rubicon and 5105.0 grams (10.0 eqs) Terrathane 1000 from Dupont. Table I shows the results.

20      Preparation of Curative Blend (Part B)

The same procedure used to prepare the Part B of Example I was used with the components listed below.

	<u>Ingredients</u>	<u>Parts by Weight (grams)</u>	<u>Equivalents</u>
25	Terrathane 1000, Dupont	964.8	1.890
	Voranol XAS1077.02, Dow	688.9	0.630
	1,4 butanediol	255.5	5.670
	DETDA, Ethyl	157.5	1.770
	PDI 47055-B, PDI	86.5	0.035
30	Coscat 83, Cosan	1.3	---
	Baylith L Powder, Mobay	38.8	---

The Part A and Part B from each example were combined 1:1 by volume and sprayed using the equipment previously described. Table I shows the results.

TABLE I

1	<u>Part A</u>	<u>Example I</u>	<u>Example II</u>
	%NCO	19.7	18.7
	Visc @ 75°F, cP	600	900

5

Part B

	%H <sub>2</sub> O, KF	0.08	0.09
	Visc @ 75°F, cP	600	800

Physical Properties of Spray-Applied, 1:1 Volume Mix

10

Aged 14 Days at 75°F/50% R.H.

	Hardness	60 Shore D	90 Shore A
	Tensile, psi	3500	3000
	Elongation, %	120	320
	Tear, DieC	500	400
15	Resilience, Bashore	30	27
	Abrasion Resistance,		
	Wt. loss, mg.		
	(H-10 Wheel/1000g/1000r)	50	40
	Elcometer Adhesion, psi		
	(unprimed cold-rolled steel)	1800	1500

20

Numerous variations can be made in the practice of the invention, by selecting particular polyisocyanate, polyisocyanurate or isocyanate-terminated prepolymers or quasi-prepolymers and combinations thereof, and by selecting particular curative components comprised of

25 particular polyamines or alkanolamines, particular glycols, particular high molecular weight polyols or polyamines, particular moisture-adsorbing additives, particular catalysts and any other desired additives or fillers, to establish the specific physical and chemical

30 characteristics and economics of use appropriate for the surface to be coated.

35

## I CLAIM:

1        1. A two-component solventless spray composition for producing polyurethane and poly(urea)urethane coatings comprised of substantially equal volumes of:

5                an isocyanate-containing component comprised of a liquid polyisocyanate, polyisocyanurate or isocyanate-terminated prepolymer or quasi-prepolymer; and

10                a curative component comprised of from about 0% to about 15% by weight of one or more polyamines or alkanolamines in an amount sufficient to react to form a thixotropic mixture about 15 seconds to about 2 minutes after being mixed with the isocyanate-containing component, from about 10% to about 20% by weight of one or more glycols having an equivalent weight in the range from about 30 to about 200, from about 40% to about 80%  
15                be weight of one or more high molecular weight polyols or polyamines having an equivalent weight in the range from about 300 to about 2000, and at least about 1% by weight of one or more additives to adsorb moisture or carbon dioxide.  
20

2. A composition as set forth in claim 1 wherein the polyamines or alkanolamines have an equivalent weight in the range from about 30 to about 200.

25        3. A composition as set forth in claim 1 wherein the curative component is also comprised of one or more catalysts to promote the hydroxyl-isocyanate reaction in formation of a polyurethane or poly(urea)urethane.

30        4. A composition as set forth in claim 1 wherein the additives to adsorb moisture are selected from the group consisting of calcium sulfate, calcium oxide or synthetic zeolite molecular sieves.  
35

1           5. A composition as set forth in claim 3 wherein the  
catalysts are selected from the group consisting of  
dibutyltin dilaurate, stannous octoate, lead octoate,  
phenylmercuric propionate, ferric acetylacetonate,  
5           organo-tin carboxylates, organo-bismuth compounds or  
organo-zinc compounds such as zinc octoate.

          6. A composition as set forth in either of claims 1  
or 3 wherein the components when blended have an average  
10           equivalent weight of from about 150 to about 500.

          7. A composition as set forth in either of claims 1  
or 2 wherein the components have an isocyanate to active  
hydrogen equivalent ratio of from about 0.85 to about  
15           1.15.

          8. A composition as set forth in claim 1 wherein  
each component has a viscosity less than 1000 centipoise  
at 70°F.

20           9. A composition as set forth in claim 1 wherein the  
one or more polyamines or alkanolamines make up from  
about 2% to about 7% by weight of the curative component.

25           10. A composition as set forth in claim 1 wherein the  
one or more polyamines or alkanolamines are diethyl  
toluenediamine.

30           11. A composition as set forth in claim 1 wherein the  
isocyanate-containing component is based on aliphatic  
isocyanate and the polyamine or alkanolamine is a very  
reactive aliphatic or cycloaliphatic polyamine.

1        12. A composition as set forth in claim 1 wherein the  
isocyanate-containing component is based on aromatic  
diisocyanate and the polyamine or alkanolamine is an  
aromatic diamine.

5        13. A composition as set forth in claim 1 wherein the  
one or more additives to adsorb moisture or carbon  
dioxide make up from about 1% to about 20% by weight of  
the curative component.

10       14. A two-component solventless spray composition for  
producing polyurethane and poly(urea)urethane coatings  
comprised of:

15       an isocyanate-containing component comprised of a  
liquid polyisocyanate, polyisocyanurate or isocyanate-  
terminated prepolymer or quasi-prepolymer; and

20       a curative component comprised of from about 0%  
to about 15% by weight of one or more polyamines or  
alkanolamines in an amount sufficient to form a coating  
which is substantially tack-free within about 5 minutes  
to about 60 minutes after being mixed with the  
isocyanate-containing component, from about 10% to about  
20% by weight of one or more glycols having an equivalent  
weight in the range from about 30 to about 200, from  
25       about 40% to about 80% by weight of one or more high  
molecular weight polyols or polyamines having an  
equivalent weight in the range from about 300 to about  
2000, and from about 1% to about 20% by weight of one or  
more additives to adsorb moisture or carbon dioxide.

30       15. A two-component solventless spray composition for  
producing polyurethane and poly(urea)urethane coatings  
comprised of:

1 an isocyanate-containing component comprised of a  
liquid polyisocyanate, polyisocyanurate or isocyanate-  
terminated prepolymer or quasi-prepolymer; and

5 a curative component comprised of from about 2%  
to about 7% by weight of one or more polyamines or  
alkanolamines having an equivalent weight in the range  
from about 30 to about 200, from about 10% to about 20%  
by weight of one or more glycols having an equivalent  
weight in the range from about 30 to about 200, from  
10 about 40% to about 80% by weight of one or more high  
molecular weight polyols or polyamines having an  
equivalent weight in the range from about 300 to about  
2000, and from about 1% to about 20% by weight of one or  
more additives to adsorb moisture or carbon dioxide.

15 16. A method for the solventless spray application of  
a polyurethane or poly(urea)urethane coating, comprising  
the steps of:

20 delivering to a manifold an isocyanate-containing  
component comprised of a liquid polyisocyanate,  
polyisocyanurate or isocyanate-terminated prepolymer or  
quasi-prepolymer;

25 delivering to said manifold a curative component  
comprised of from about 0% to about 15% by weight of one  
or more polyamines or alkanolamines having an equivalent  
weight in the range from about 30 to about 200, from  
about 10% to about 20% by weight of one or more glycols  
having an equivalent weight in the range from about 30 to  
about 200, from about 40% to about 80% by weight of one  
or more high molecular weight polyols or polyamines  
30 having an equivalent weight in the range from about 300  
to about 2000, and from about 1% to about 20% by weight  
of one or more additives to adsorb moisture or carbon  
dioxide;



1 mixing the isocyanate-containing component and  
the curative component with each other; and

5 spraying the resulting mixture through an  
atomizing nozzle onto a surface to produce a polyurethane  
or poly(urea)urethane coating.

10 17. A method as set forth in claim 16 wherein the  
isocyanate-containing component and the curative  
component are delivered to the manifold in a volumetric  
ratio of 1:1.

15 18. A method as set forth in claim 16 wherein the  
average equivalent weight of the resulting mixture is in  
the range of from about 150 to about 500.

20 19. A method as set forth in claim 16 wherein the  
isocyanate-containing component and the curative  
component each have viscosities less than 1000 centipoise  
at ambient temperatures.

25 20. A method as set forth in claim 16 wherein the one  
or more additives to adsorb moisture or carbon dioxide  
make up from about 2% to about 8% by weight of the  
curative component.

30 21. The product of any of the methods set forth in  
claims 14-20 inclusive.

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# INTERNATIONAL SEARCH REPORT

International Application No PCT/US87/01216

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>3</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC (4); C08L 75/04		
U.S. CL. 528/55		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>4</sup>		
Classification System	Classification Symbols	
U.S.	528/55, 56, 57, 58, 60, 61, 64, 65, 66, 75, 76, 77	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>5</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup>		
Category <sup>*</sup>	Citation of Document, <sup>15</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>
A	US, A, 4,257,299 (OECHSLE) 12 MAY 1981	1-21
A	US, A, 4,195,148 (HAGEN) 25 MARCH 1980	1-21
A	US, A, 4,234,445 (HAGEN) 18 NOVEMBER 1980	1-21
<p><sup>*</sup> Special categories of cited documents: <sup>14</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the International filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the International filing date but later than the priority date claimed</p> <p>"T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search <sup>2</sup>	Date of Mailing of this International Search Report <sup>2</sup>	
19 AUGUST 1987	08 SEP 1987	
International Searching Authority <sup>1</sup>	Signature of Authorized Officer <sup>20</sup>	
ISA/US	M. J. WELSH 	